This paper shows that the symmetry breaking effects involved in chemisorbing \( \pi \)-stacked benzene rings to metallic electrodes can have a significant impact on the transport properties. Fully eclipsed stacks may not be optimal; rather stacks designed to favor interactions between particular sites lead to increased transport. Conversely, in the case of transport through an infinite stack of benzene rings, where the full 6-fold symmetry of the system is preserved, maximal overlap of the rings in the fully eclipsed structures maximizes transport.

Molecules have been investigated for use as electronic components in two contexts. Molecular electronics has looked at single molecules bound in junctions to (often) metallic electrodes. Conversely, organic electronics has focused on molecular films as active layers, often in organic transistors or photovoltaics. While the relationship between chemical structure and electronic functionality may be, in many cases, transferable between these two contexts, we show that this is not always the case. The properties of a molecular structure employed in these different environments can be influenced significantly by the nature of the connection to the leads.

All transport calculations were performed using gDFTB,\(^1\)\(^-\)\(^5\) although some of the results are reproduced in the Supporting Information using density functional theory in combination with an exchange-correlation functional specifically suited to intermolecular interactions. In both cases these methods provide a description of the coherent tunneling regime and consequently any departure from this in real systems (such as sequential incoherent hopping steps) will not be captured. The calculation details are included in the Supporting Information.

A series of \( \pi \)-stacked molecules with thiol substituents for binding to gold electrodes is shown in Figure 1. The systems are designated with a number (1, 2, or 3) indicating how many phenyl rings are present and a letter (P or M) indicating whether the electrodes are attached with either \textit{para-} or \textit{meta-}type substitution. These systems can be considered as even alternant hydrocarbons,\(^6\) with stars placed on every second atom and with no nearest neighbors being either both starred or unstarred. In the case of the stacked systems, the starring continues across nearest neighbors in the stack as has been discussed previously in the case of magnetic systems.\(^7\)

When the terminal sulfurs are both starred, this indicates \textit{“alike”} coupling and is known to result in weak transmission with \textit{meta-}substituted benzene being the prototypical example. The alternative is \textit{“disjoint”} coupling, which leads to high levels of transport, with \textit{para-}substituted benzene being the counterpart example. The spin coupling in biradical molecules similar to 2P and 2M (with radical substituents in the place of the binding groups) has been measured\(^8\)\(^,\)\(^9\) with a high-spin ground state observed in the \textit{“para”} substituted system and low-spin ground state for the \textit{“meta”} substituted system.

In single molecule transport, \textit{alike} coupling provides destructive interference features, frequently near the Fermi energy of the electrodes, and, consequently, a significant reduction in the observed current. The electronic transmission as a function of the electron injection energy for the molecules in Figure 1 is shown in Figure 2. In each case the gold Fermi energy (which we set to \(-5.0\) eV) is marked with a dashed line.

While the interference in the \( \pi \)-system transport through 1M is not evident in the total transmission, due to the residual \( \sigma \)-system transport, a pronounced interference feature is evident near the Fermi energy in 2P and 3M. Consequently, there is lower transport through 2P than 2M in this region, a result that might at first appear unintuitive if the differences between \textit{“meta”} and \textit{“para”} substitution were naively extended to stacked systems. This relationship is reversed again in 3P and 3M with the same trend as the single molecule systems.

By appreciating that the starring assignments across the stack are set by which sites are nearest neighbors, it is possible to design structures with spatial dislocation between the rings in 2P and 2M, making both systems exhibit \textit{disjoint} coupling. Figure 3 shows two structures (2P \textit{max.} and 2M \textit{max.}) where spatial dislocation is used to favor overlap between selected sites, rather than overlap of the

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**Figure 1.** A series of thiol-substituted benzene systems for transport calculations with gold electrodes. The systems are all even alternant hydrocarbons and are marked with stars to show when alike (low) or disjoint (high) coupling is expected. In each case, adjacent layers are colored differently for clarity.

**Figure 2.** Transmission through the \( \pi \)-stacked molecules in Figure 1. The Fermi energy is marked with a dashed line.
with the transmission through\(\alpha\), which is shown in Figure 5 and confirms the behavior hypothesized from the starring arguments. In the fully eclipsed (six nearest-neighbor interactions across the stack) and the dislocated structures favor select sites leading to higher transmission and a simpler picture of the local contributions.

In organic electronics, where molecules are not generally chemisorbed through binding groups to the electrodes, electronic coupling matrix elements are generally calculated rather than electronic transmission. The comparison of these two approaches can be made directly for \(\pi\)-stacked systems; however here we simply study analogous systems relevant in the context of organic electronics. To see the influence of the symmetry breaking, the transport through four systems of benzene rings, without metallic electrodes, was considered. The structures of these systems are shown in Figure 6 and have been chosen to highlight the role of nearest neighbor coupling in these stacks. The systems range from the fully eclipsed (six nearest-neighbor interactions across the stack) to a system with significantly reduced spatial overlap (one site and two site nearest neighbor interactions across the stack). These systems were calculated with periodic boundary conditions, and parts of the stack are used to constitute the "electrodes" and the "molecule" for the purposes of the formalism; full details are given in the Supporting Information.

The transmission through these systems is shown in Figure 7, and it is immediately clear that the transport characteristics differ substantially from the systems bound to metallic electrodes. The transmission is plotted on a linear scale as the off-resonant transport near the Fermi energy that characterizes the measurable range in molecular junctions is essentially nonexistent. In the molecular junction, the nonzero density of states in the gold electrodes allows for electronic injection over a wide range between the molecular resonances. Conversely, when the system is comprised of molecules alone there are bands of transmission that emerge from the mutual broadening of the molecular resonances, but this broadening occurs over a relatively limited range. As distinct from calculations in molecular junctions where transmission rarely exceeds unity by any appreciable extent, the resonant bands in these systems show transmission peaking at two over a considerable range. In all of the dislocated systems the range over which the resonant transmission reaches its local maximum is significantly reduced as compared with the fully eclipsed structures. While this is in contrast with the off-resonant behavior in the molecular
junctions, where dislocation increased transmission, it is in keeping with the trends observed for the resonant transport as well as those observed in prior work on electron transfer.  

Finally, it is possible also to plot the local transmission through these systems, shown in Figure 8. This reveals the simplicity and high symmetry of the local transmission through the eclipsed structure, an image in accordance with an intuitive picture of the electronic interaction between two stacked benzene rings. The dislocated structures show transmission predominantly through the sites with maximum spatial overlap but also more complicated features. In contrast with the symmetry broken systems in molecular junctions, spatial dislocation leads neither to increased transport nor to simplicity in the patterns of the local transport.

Transport through π-stacked systems offers a rich array of properties for future study. The effects of symmetry breaking in these systems cannot be ignored as they have a direct bearing on the nature of the electronic coupling and the favored interactions in the resulting structures. Systems that may be ideal candidates for single molecule studies in transport junctions may be unsuitable as components of an active organic film, and the converse may also hold true. The nature of the charge injection into the stacked systems will influence the role that symmetry plays and therefore should be carefully considered in molecular design.

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Supporting Information Available: Full details of calculation method, calculations using density functional theory, geometries of the molecular systems used in all calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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